Modeling Migration-Diffusion-Reaction Processes in an Idealized Lithium-Sulfur Cell

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Abstract

During the basic operation of a lithium-sulfur (Li-S) cell, sulfur molecules are required to undergo a complex mix of electrochemical and chemical reaction processes. To date, almost all modeling of Li-S cell behavior has been undertaken using electroneutral, structurally homogenized, cell scale models which account for most of these processes. However, these models necessarily simplify the electrolyte structure at the interface between the electrolyte and electrode surfaces, known as the electric double layer (EDL). Furthermore, the full reaction process is typically reduced to two or three linear electrochemical steps and a similar number of dissolution/precipitation steps.

We describe here work which we have undertaken in order to try and understand whether relaxing some of the constraints of the homogenized models, most importantly that of electroneutrality, can help us better understand reaction processes in systems similar to a Li-S cell. By accounting for the EDL, surface interactions can be better described, including the effects of relative species sizes in the liquid phase. However, due to a significant resultant growth in model complexity, the cost of doing this is that it is necessary to simplify the cell geometry to that of a slit-pore. The model describes species transport in the electrolyte phase, using a modified form of the Nernst-Planck equation coupled to the Poisson equation, and accounts for both heterogeneous surface reactions (e.g. chemical precipitation and electrochemical oxidation/reduction) and homogeneous bulk phase chemical reactions (e.g. dissociation/association) in the bulk phase of the electrolyte.

We find that it is possible to recreate some of the trends seen in the discharge curve for a Li-S cell, for example the two-step voltage profile during cell discharge (Figure 1), even in the absence of some of the processes to which they are commonly attributed, most notably the precipitation of species produced towards the end of discharge. However, in agreement with Zhang et al. [1], the precipitation and dissolution processes do appear to be required in order to account for the long voltage plateau observed experimentally in the second step of the discharge.

The model is solved using General Form PDE interface and Electrostatics interface of COMSOL Multiphysics®, together with the Events interface for controlling operational parameters. Furthermore, we also use LiveLink™ for MATLAB® to construct the large number of supporting equations for the model, in order to assist with rapid model iterations, and to help post-process the resulting data.

Reference

[1] T. Zhang et al., Modelling the voltage loss mechanisms in lithium-sulfur cells: the importance of electrolyte resistance and precipitation kinetics, Phys. Chem. Chem. Phys., Vol. 17, pp. 22581-22586 (2015)

Figures used in the abstract

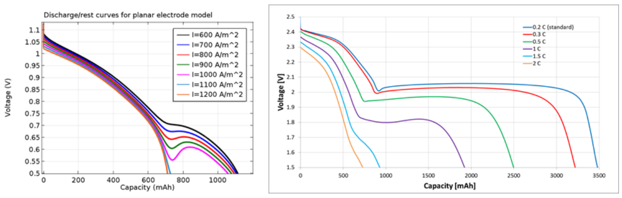

Figure 1: Figure 1: Comparison of trends in the voltage profile of the model cell (left) and a real cell (right) during discharge as a function of current. While the model predicts a two-step discharge profile, the extended second step is not predicted unless precipitation is accounted for. The working voltage of the model cell has been lowered to reduce numerical instability.